

# The Analysis of Perchlorate by Ion Chromatography/Mass Spectrometry

## Application

Environmental

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### Abstract

**A method for the determination of perchlorate anion at sub ppb levels using ion chromatography/mass spectrometry (IC/MS) is described. The IC/MS method follows EPA Method 314 methodology originally developed for IC with conductivity detection at the single ppb range [1]. The IC/MS method is not affected by the addition of the interference matrix described in Method 314 on perchlorate recoveries throughout the measurable range. Typical recoveries are 90%–105% at the 0.5 and 1-ppb level in synthetic drinking and waste waters with the method detection limit (MDL) less than 100 ppt.**

### Introduction

Perchlorate is commonly used as an oxidant in solid fuel propellants for rockets and missiles. Recently, perchlorate contamination was found in many aquifers associated with the Colorado River (CA). Other sites were also identified, but by far the widest contamination problem is in California, Nevada, and Arizona. Perchlorate was also found at elevated levels in crops that use contaminated water for irrigation.

IC with conductivity detection can be used to measure perchlorate levels in drinking and waste waters (as per EPA Method 314). The method is reliable to approximately 1–5 ppb in drinking water, but sensitivity decreases dramatically as the complexity of the matrix is increased (such as in surface and waste waters). Both false positive and false negative results may occur due to matrix effects and coeluting substances detected by non-specific conductivity detection. Lower detection limits (DLs) for perchlorate are needed as the EPA and state environmental agencies are looking to target levels in the 1–2 ppb range. Reliability of the measurement in heavy matrix samples is also important.

The use of a mass spectrometer as a detector for perchlorate at much lower DLs (50–100 ppt) has shown promise, but reliability issues and problems related to suppression of the electrospray ionization (ESI) signals in typical matrices are well documented phenomena. The key to reducing suppression is to ensure that analyte and high concentrations of matrix are well separated and do not enter the ion source and interface at the same time.



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In addition to ion suppression in the source, the  $m/z$  attributed to perchlorate anion (99 and 101) have isobaric interferences which can be attributed to minor sulfate isotopes and from organic material that can be present and bleed from the column used for ion chromatography (IC) and the associated cation suppressor. The selection of separation column and suppressor are critical for reduction of sample bleed and for efficient separation of high levels of interfering ions, particularly sulfate.

### Precautions Peculiar to Ion IC/MS

The use of nonvolatile buffer systems is usually avoided when performing ESI or with any atmospheric pressure ionization (API) technique. Some IC mobile phase reagents (such as strong inorganic acids) are not suited for direct introduction into API sources. The operator must be certain to avoid mobile phases that are not compatible with the stainless steel parts of the mass spectrometer. To avoid inorganic salt build-up it is essential that a suppressor, unique to the IC technique, be employed. The suppressor removes cations from the eluent stream, after the separation column, and replaces them with a proton. Accumulation in the API source of salts from the mobile phase and any dissolved solids in the sample is eliminated. During system equilibration, prior to adding the suppressor to the flow path, it is important that the effluent from the IC be diverted by the integral valve of the 1100 MSD (mass selective detector) and not directed to the ESI source. This eliminates the possibility of any sodium hydroxide or other mobile phase constituent from entering the source while the suppressor system is equilibrating or otherwise offline. Should a contaminating solution be introduced to the source, the MS system should be vented and surfaces up to and including the glass capillary should be cleaned. This will recover the performance lost due to NaOH introduction.

### Instrumental and Operating Parameters

The analytical system consists of a modular ion chromatograph (Metrohm-Peak, Inc.) and an 1100 MSD SL Quad (Agilent Technologies, Inc.). A standard electrospray interface was used. The two systems were synchronized by use of contact closure between the chromatographic autosampler and the mass spectrometer. A complete list of instrumental parameters is listed in Table 1. A list of Metrohm-Peak ion chromatograph parameters and setup appear in Table 2.

**Table 1. Operating Parameters**

<b>Metrohm Advanced IC</b>	
Injection loop size	100 $\mu$ L
Column	MetroSep ASUPP-5 (4 mm $\times$ 100 mm)
Eluent	3/7 v/v MeOH/30 mM NaOH
Flow rate	0.8 mL/min
<b>Agilent 1100 MSD</b>	
Tune mode	Negative mode "auto-tune"
$V_{cap}$	1400 V
Drying gas flow and temperature	9 L/min @ 320 $^{\circ}$ C
Nebulizer pressure	20 psig
Fragmentor	140 V
Dwell time $m/z$ 99	1 s
Dwell time $m/z$ 101	1 s

**Table 2. Metrohm-Peak Ion Chromatograph Parameters and Setup**

<b>Hardware</b>	
Metrohm Advanced IC consists of Metrohm 788 Autosampler, 830 Interface with ICNet 2.3 software, 833 Suppressor Module, 819 Advanced IC Detector, 820 IC Separation Center, 818 IC serial dual-piston pump	
<b>Setup</b>	
Column	Metrohm ASUPP-5 – 100 (4 mm $\times$ 100 mm) p/n 6.1006.510
Eluent	3/7 v/v MeOH/30 mM NaOH
Regenerant solution	5/95 v/v MeOH/60 mM HNO <sub>3</sub>
Rinse solution	5/95 v/v MeOH/H <sub>2</sub> O
Flow rate	0.8 mL/min
Suppressor regenerant and rinse flow rate	0.5 mL/min
Connection to synchronized start MSD and IC by MSD-com port and events on 820 IC separation center.	

Instrumental parameters for the analysis of perchlorate by IC/MS were initially chosen to reduce or eliminate suppression due to coelution of matrix and analyte ions, and to reduce the effective concentration of matrix in the electrospray interface. Choosing operating conditions in this way increased reliability and stability of the system but at the cost of potential sensitivity.

To reduce matrix suppression, a 4-mm id column was chosen over a 2-mm id column. The larger diameter column reduces the effective concentration of matrix in the system by dilution effects. The larger id column also allowed a 100- $\mu$ L injection, as used for this work, and a larger injection volume can easily be accommodated. Capacity of the column is also far greater than smaller id columns,

resulting in improved peak shape of any matrix or high concentration materials and reduced tailing into the analyte peak. All of these factors ensure that the majority of the matrix is well separated from the analyte for reduction or elimination of suppression effects.

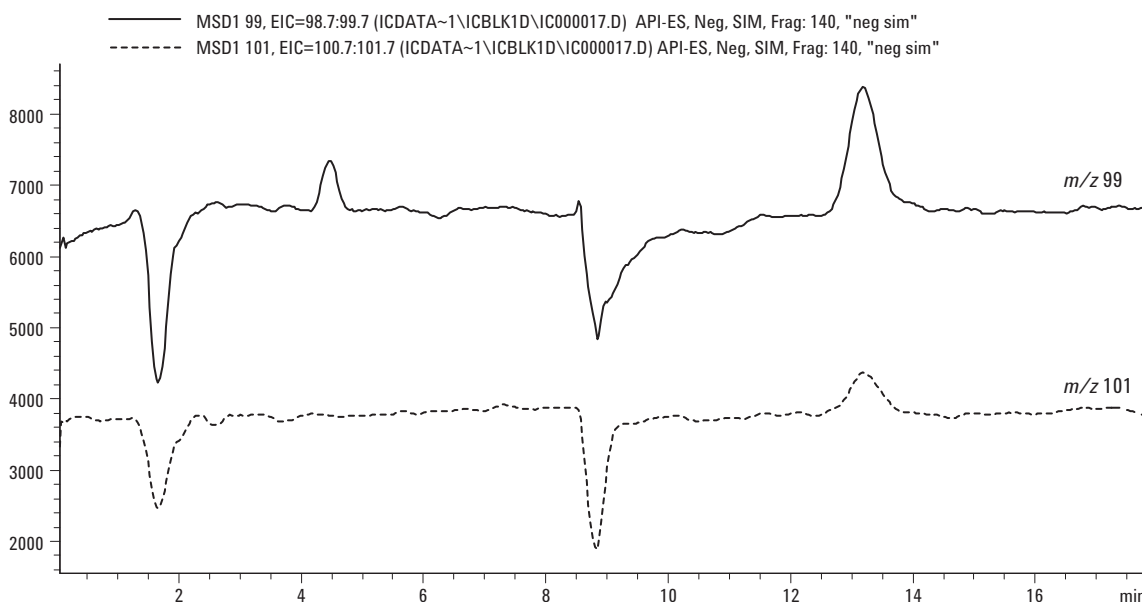
In addition to the ion exchange column used for the separation, a suppression column is also used to eliminate any sodium and calcium in the sample matrix. While not a direct problem with the detection of analyte, the presence of these involatile cations would accumulate in the interface from mobile phase and when high total dissolved solids (TDS) samples are analyzed. This would interfere with the long-term stability of the system. Complete removal of the metal cations also decreases the risk of suppression by ensuring that only protonated anions enter the mass spectrometer interface.

The 1100 MSD ESI interface is designed for relatively high flows while maintaining high sensitivity, here to reach DLs less than 100 ppt. Many ESI interfaces are extremely flow sensitive and do not

perform well at flows typical for 4-mm id columns. The 1100 MSD ESI interface performs best at low flows but does not show the same drastic decrease in sensitivity at higher flow as observed with other interfaces.

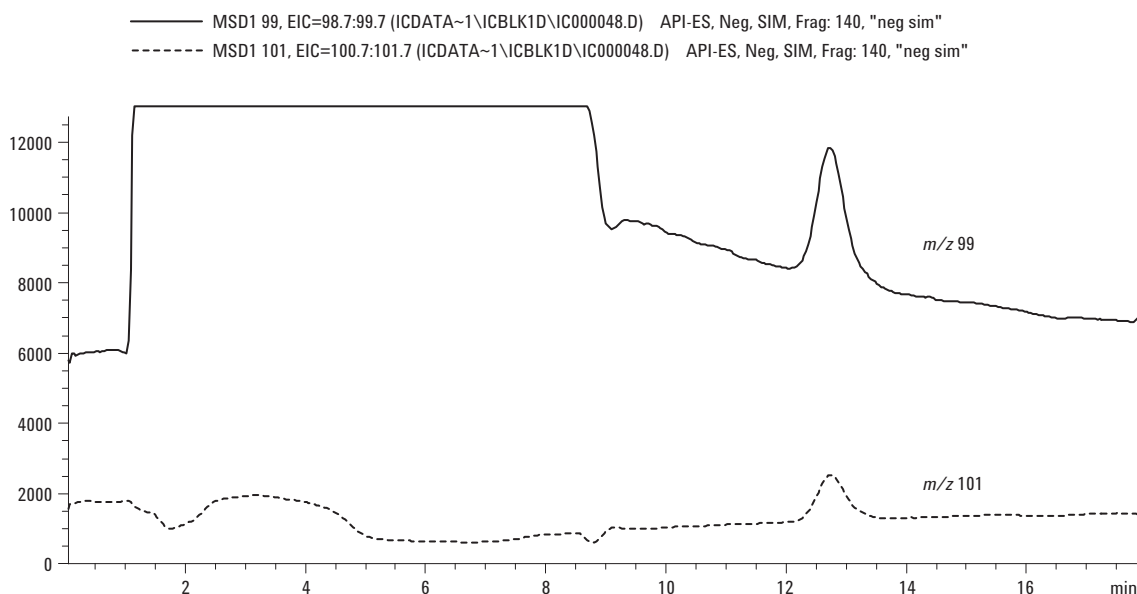
## Results

The IC/MS trace of a 500 ppt perchlorate standard is shown in Figure 1. It shows excellent signal-to-noise (S/N) for perchlorate ( $m/z$  99), eluting at a retention time (RT) of about 13 minutes. The Metrohm-Peak IC uses a combination of three suppressors that can be changed during a run to ensure that any one suppressor does not become saturated with cations. While one suppressor is in operation another is reconditioning and the third is rinsing with ultrapure water. The abrupt signal changes observed at 1.5 and 9 minutes are due to ultrapure water entering the flow path from the rinsed suppressor during automated operations of the suppression column system.



**Figure 1.** Single ion chromatograms for 0.5-ppb perchlorate standard for  $m/z$  99 and 101.

Sequentially changing and reconditioning the suppressors during the analysis is extremely important in the analysis of high matrix samples. Figure 2 shows  $m/z$  99 and 101 traces for 1-ppb perchlorate in a 1000-ppm matrix of sulfate, chloride, and carbonate. Early in the chromatogram the effect of the matrix can be clearly seen as both interference at the monitored mass as well as suppression of the signal in general. The suppressor change at 9 minutes ensures that a clean suppressor is in place for the perchlorate ion. This results in a very clean signal for perchlorate at about 13 minutes.



**Figure 2.** Single ion chromatograms for 1000 ppm each of  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  in Matrix + 1-ppb perchlorate ( $m/z$  99 and 101).

Figures 3 and 4 show the calibration data for both  $m/z$  99 and 101 for perchlorate from 0.1 to 5 ppb. Calibration at both masses is linear over the measured range.

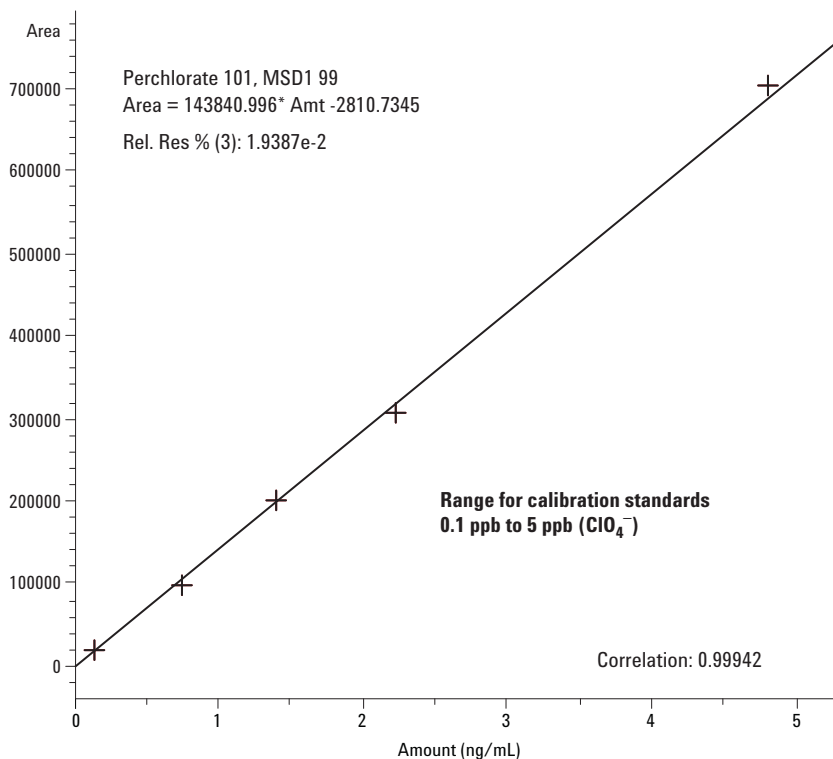


Figure 3. Calibration data ( $m/z$  99).

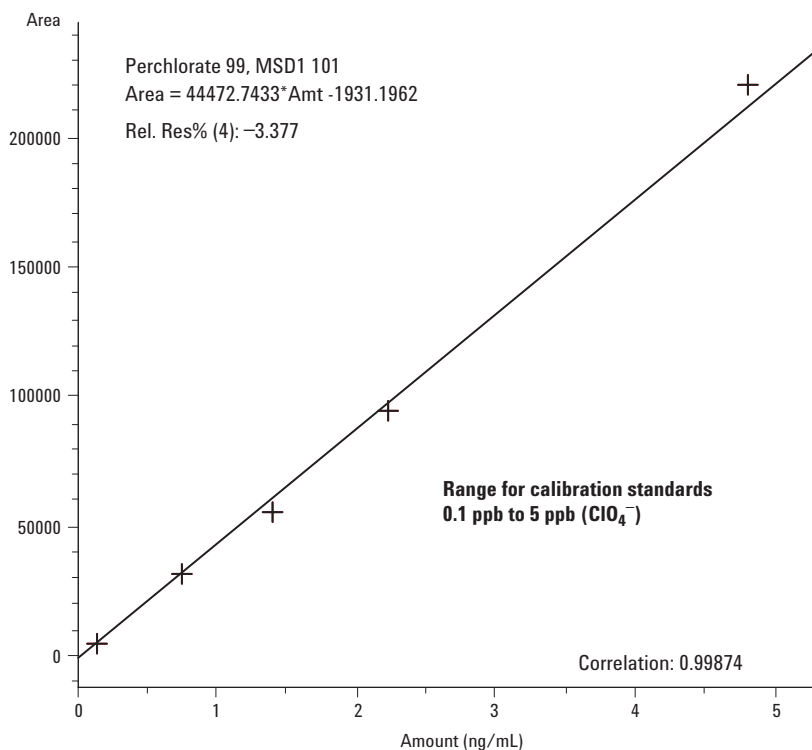
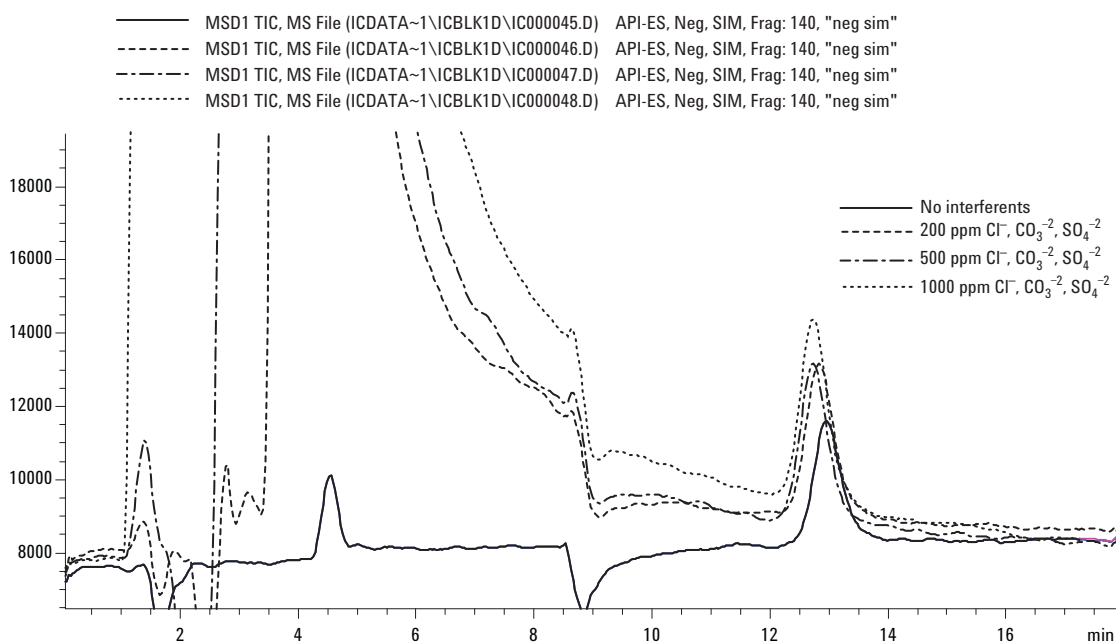


Figure 4. Calibration data ( $m/z$  101).

Figure 5 shows the  $m/z$  99 single ion chromatograms for a set of matrix spikes each containing a 1-ppb perchlorate. A small RT change is noted for perchlorate between a perfectly clean standard and the matrix additions. This small shift is normal for IC due to initial overloading of the separation column. It does not interfere with the identification or determination of perchlorate. If desired, the RT shift between standards and matrix-laden samples can be avoided by using standards prepared with a limited amount of matrix.



**Figure 5. Synthetic matrix spikes overlaid with 1-ppb perchlorate standard.**

Table 3 shows the results from replicate injections of perchlorate spikes at 0.49 and 0.78 ppb in deionized water. Recoveries for analysis using both ions are excellent, as expected in clean matrix. Precision is also quite good for both ions at these levels.

**Table 3. Results of Water Fortified with Perchlorate at 0.48 and 0.78 ppb**

<b>Nominal Sample ID ppb</b>	<b>Actual conc., ppb</b>	<b>Detected conc., ppb <i>m/z</i> 99</b>	<b>% Recovery <i>m/z</i> 99</b>	<b>Detected conc., ppb <i>m/z</i> 101</b>	<b>% Recovery for <i>m/z</i> 101</b>	<b>0.48-ppb Replicates</b>
0.5	0.480	0.487	101.46	0.519	108.13	
0.5	0.480	0.477	99.38	0.471	98.13	
0.5	0.480	0.460	95.83	0.490	102.08	
0.5	0.480	0.477	99.38	0.492	102.50	
0.5	0.480	0.520	108.33	0.505	105.21	
0.5	0.480	0.494	102.92	0.509	106.04	
<b>Average</b>	<b>0.480</b>	<b>0.486</b>	<b>101.22%</b>	<b>0.498</b>	<b>103.68%</b>	
<b>Std. Dev</b>		<b>0.020</b>	<b>0.042</b>	<b>0.017</b>	<b>0.035</b>	
<b>RSD (%)</b>		<b>4.18</b>	<b>4.18</b>	<b>3.41</b>	<b>3.41</b>	
<b>Nominal Sample ID ppb</b>	<b>Actual conc., ppb</b>	<b>Detected conc., ppb <i>m/z</i> 99</b>	<b>% Recovery for <i>m/z</i> 99</b>	<b>Detected conc., ppb <i>m/z</i> 101</b>	<b>% Recovery for <i>m/z</i> 101</b>	<b>0.78-ppb Replicates</b>
1.0	0.780	0.756	96.92	0.768	98.46	
1.0	0.780	0.810	103.85	0.830	106.41	
1.0	0.780	0.776	99.49	0.772	98.97	
1.0	0.780	0.799	102.44	0.754	96.67	
1.0	0.780	0.788	101.03	0.768	98.46	
1.0	0.780	0.792	101.54	0.807	103.46	
<b>Average</b>	<b>0.780</b>	<b>0.787</b>	<b>100.88%</b>	<b>0.783</b>	<b>100.41%</b>	
<b>Std. Dev.</b>		<b>0.019</b>	<b>0.024</b>	<b>0.029</b>	<b>0.037</b>	
<b>RSD (%)</b>		<b>2.40</b>	<b>2.40</b>	<b>3.70</b>	<b>3.70</b>	

Table 4 shows the results of a much more difficult test of the system, the analysis of 1-ppb spikes in three different levels of matrix prepared according to EPA Method 314. The samples were run sequentially with a blank and calibration verification run after each set of nine samples. Recoveries of analyte at the ppb level are excellent for all matrices, with an average recovery better than 95% for both monitored ions in all matrices. The recovery data in matrix shows how the system is not effected by the presence of potential interferents in the system at very high concentrations.

**Table 4. Results of Different Matrices Fortified with Perchlorate**

Sample	Perchlorate				
	Actual conc., ppb	Detected conc., ppb <i>m/z</i> 99	% Recovery <i>m/z</i> 99	Detected conc., ppb <i>m/z</i> 101	% Recovery <i>m/z</i> 101
200 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	0.780	0.799	102.44	0.784	100.51
500 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.804	80.40	0.808	80.80
1000 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.930	93.00	0.940	94.00
200 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	0.780	0.700	89.74	0.770	98.72
500 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.870	87.00	0.860	86.00
1000 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.973	97.30	0.986	98.60
200 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	0.780	0.810	103.85	0.796	102.05
500 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.851	85.10	0.846	84.60
1000 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.990	99.00	0.977	97.70
<b>Blank</b>	<b>0.000</b>	<b>0.000</b>		<b>0.000</b>	
<b>CC 1.0 ppb (No interferents)</b>	<b>0.780</b>	<b>0.747</b>	<b>95.77</b>	<b>0.742</b>	<b>95.13</b>
200 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	0.780	0.799	102.44	0.777	99.62
500 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.920	92.00	0.921	92.10
1000 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	1.000	100.00	1.040	104.00
200 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	0.780	0.860	110.26	0.830	106.41
500 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.930	93.00	0.913	91.30
1000 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	1.090	109.00	1.050	105.00
200 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	0.780	0.800	102.56	0.850	108.97
500 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	0.890	89.00	0.904	90.40
1000 ppm each of $\text{Cl}^-$ , $\text{CO}_3^{-2}$ and $\text{SO}_4^{-2}$	1.000	1.040	104.00	1.070	107.00
<b>Average (%)</b>			<b>96.67</b>		<b>97.10</b>
<b>Std. Dev.</b>			<b>0.082</b>		<b>0.080</b>



Table 5 shows recoveries data for perchlorate in other matrices. These matrices show excellent recovery where perchlorate is present and, more importantly, perchlorate was not found in samples known not to have perchlorate or in samples containing high levels of interferents known to complicate perchlorate determination when using conductivity detection.

Sample 5 in Table 5, is a waste water sample having an unknown perchlorate concentration (but less than 10 ppt) and containing very high levels of sulfonate detergents. These are known to coelute with perchlorate and give high false positive

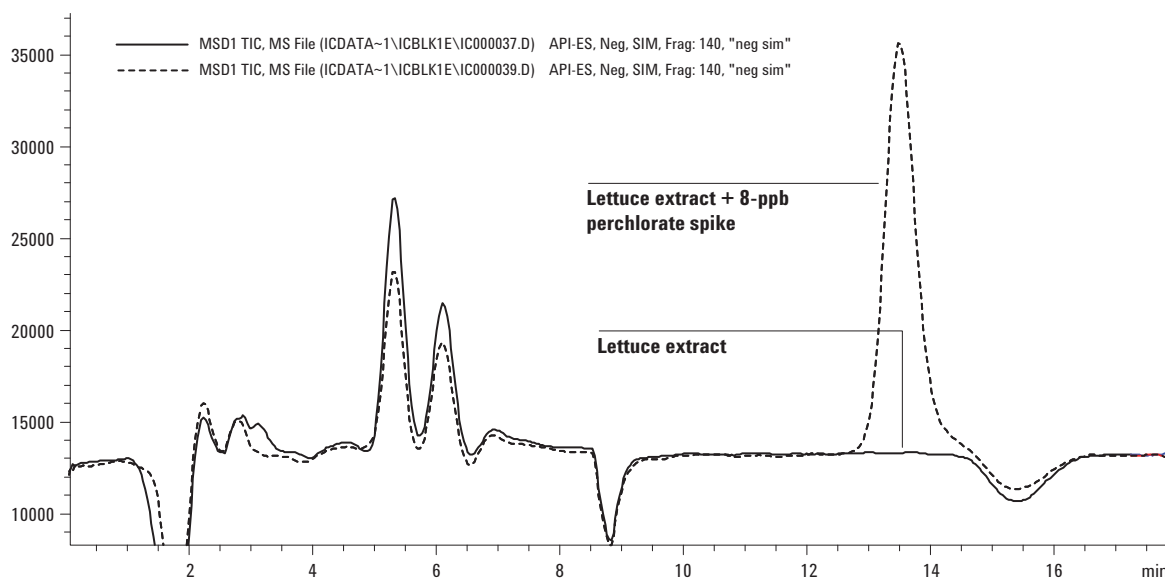
analysis (100's of ppb) when a conductivity detector is employed. The single quadrupole mass spectrometer in selected ion monitoring mode shows no signal to the detergents (of different mass than 99 or 101) and eliminates false values for samples which do not contain perchlorate.

Samples 6 and 6A, (also in Table 5) are ground waters known to contain perchlorate and a 1-ppb spike of the same sample. Samples 8 and 9 are lettuce extract showing the feasibility of the method for the analysis of vegetables. Levels in vegetables were found to be significantly higher than irrigation source waters.

**Table 5. Recoveries of Other Concentration Spikes in Various Matrices**

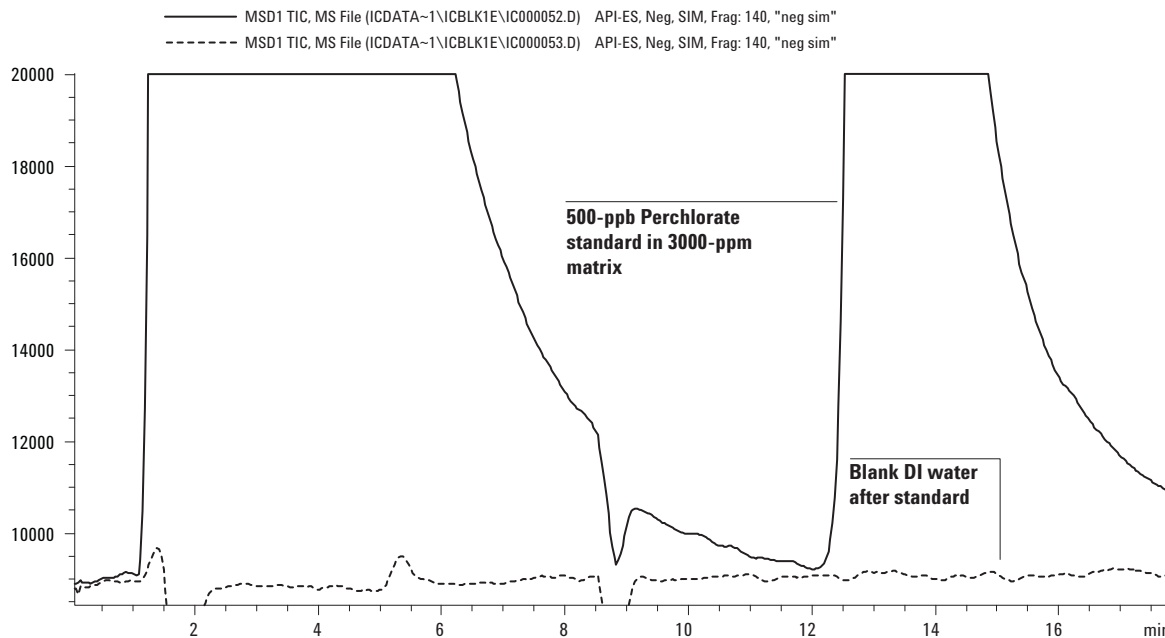
<b>Samples Submitted by Metrohm-Peak Customer</b>						
<b>Sample ID</b>	<b>Actual conc., ppb</b>	<b>Perchlorate data</b>				<b>Notes</b>
		<b>Detected conc., ppb m/z 99</b>	<b>% Recovery for m/z 99</b>	<b>Detected conc., ppb m/z 101</b>	<b>% Recovery for m/z 101</b>	
Sample-1	0.50	0.44	88.00	0.51	102.0	0.5 ppb in Distilled water
Sample-2	1.00	0.91	91.00	1.01	100.7	1.0 ppb in Distilled water
Sample-3	1.00	0.95	95.16	1.00	99.7	1.0 ppb in Tap water
Sample-4	0.42	0.41	97.33	0.43	102.1	Ground water w/0.42 ppb
Sample-5	?	0.00		0.00		Unknown value, but sample is loaded with sulfonate surfactants
Sample-6	0.35	0.30	86.93	0.33	95.0	Ground water w/0.35 ppb
Sample-6A	1.35	1.18	87.41	1.36	100.6	Sx-6 + 1 ppb spike
Sample-7	0.00	0.00	100.00	0.00	100.0	Ground water w/no perchlorate
Sample-8	0.00	0.00	0	0.00		Lettuce extract
Sample-9	7.92	7.35	92.86	7.41	93.6	Lettuce extract spike

Figure 6 shows the chromatograms of the lettuce analysis and the lack of interferences around perchlorate. The “dip” in both the blank and spike lettuce samples is due to large amounts of another eluting material going through the electrospray source, suppressing the ionization of the background signal. Conventional conductivity detection is useless for this sample as the area around perchlorate elution is overwhelmed by large amounts of coeluting material.



**Figure 6. Analysis of a lettuce extract and spike.**

Figure 7 is an example of the very low carryover of the system. A 500-ppb standard of perchlorate in high matrix was analyzed. A sequential blank after the analysis of the high standard shows no interference from either the standard or the matrix previously injected.



**Figure 7. A 500-ppb standard in high matrix followed by a sequential blank.**

## Conclusion

By using a set of instrument conditions chosen to reduce background interference and increase reliability, an isocratic IC system and a single quadrupole 1100 MSD can be very effectively used for the analysis. The analysis of perchlorate with such a system was shown to be feasible, robust, and accurate at sub ppb levels. The method also shows the feasibility and effectiveness of IC coupled to a quadrupole mass spectrometer in general. By using relatively simple method parameters and robust instrumentation, many of the difficulties previously seen with perchlorate analysis in complex matrices by IC/MS can be overcome.

## Reference

1. EPA METHOD 314.0, "Determination of Perchlorate in Drinking Water Using Ion Chromatography", Revision 1.0. November 1999, US EPA, Office of Ground Water and Drinking Water, publication 815-B-99-003  
<http://www.epa.gov/ogwdw/methods/met314.pdf>

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